

WHAT IS CLAIMED IS:

- 1 1. A method for making an inorganic/organic hybrid nanolaminate barrier film,  
2 comprising:  
3 combining an alkoxide, an alcohol, water dilute HCl and heating the resulting  
4 mixture. Introducing a coupling agent to the mixture,  
5 introducing a surfactant to the mixture in a quantity sufficient that the initial  
6 surfactant concentration is below the critical micelle concentration;  
7 adding to the mixture one or more polymer precursors suitable for the formation of a  
8 polymer selected from the group of, polyethylene naphthalate (PEN), polyether  
9 etherketone (PEEK), polyether sulfone (PES), fluorinated or non-fluorinated styrene  
10 polymer precursors, fluorinated or non-fluorinated methyl styrene polymer precursors,  
11 fluorinated or non-fluorinated (meth)acrylate polymer precursors, and combinations  
12 and/or derivatives of two or more of these precursors;  
13 adding a cross-linker agent and an initiator to the mixture;  
14 coating a substrate with the mixture; and  
15 allowing the alcohol to evaporate so that the sol forms a film having alternating  
16 organic and inorganic layers.
  
- 1 2. The method of claim 1 further comprising incorporating one or more hydrophobic  
2 groups into the polymer precursors or eliminating one or more hydrophobic groups  
3 from the polymer precursors to increase and/or decrease the hydrophobicity of the  
4 organic layers.
  
- 1 3. The method of claim 2 wherein the one or more hydrophobic groups are selected from  
2 the group of non-polar hydrophobic groups, methyl groups, benzyl (aromatic) groups,  
3  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{I}^-$ ,  $\text{SC}_n^-$  anions,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  
4  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  cations, tryptophan, isoleucine, phenylalanine, tyrosine, leucine,  
5 valine, methionine, alanine
  
- 1 4. The method of claim 3 wherein the surfactant includes one or more Gemini  
2 surfactants.

- 1 5. The method of claim 1 wherein the alkoxide includes tetraethylorthosilicate
- 2 (Si(OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> and the alcohol is ethanol..
- 1 6. The method of claim 5 wherein in molar ratios of the tetraethylorthosilicate, ethanol,  
2 water, and HCl are present in the mixture in molar ratios of 1:3.8:1:5X10<sup>-5</sup>  
3 respectively.
- 1 7. The method of claim 6, wherein the coupling agent is 7-octenyltrimethoxysilane, or  
2 methacryloxypropyl trimethoxysilane.
- 1 8. The method of claim 7 wherein the surfactant is cetyltrimethylammonium bromide.
- 1 9. The method of claim 1 wherein the one or more polymer precursors include 2,6-  
2 Dimethylnaphthalene, or a set of monomers such as bisphenol A and di-*para*-  
3 fluorophenylsulfone.
- 1 10. The method of claim 1, further comprising annealing the film at a temperature of  
2 about 125° to about 150°C or greater and/or below the lowest decomposition  
3 temperature of any of the organic materials in the film.
- 1 11. The method of claim 1 wherein coating a substrate with the mixture includes  
2 depositing the mixture on the substrate by dip coating, spin coating, spray coating,  
3 web coating, or microgravure web coating.
- 1 12. An inorganic/organic hybrid nanolaminate barrier film, comprising:  
2 a plurality of layers of an inorganic material; and  
3 a plurality of layers of an organic material chosen from the group of polyethylene  
4 naphthalate, polyether etherketone, polyether sulfone, polymers formed from  
5 fluorinated or non-fluorinated styrene polymer precursors, fluorinated or non-  
6 fluorinated methyl styrene polymer precursors, fluorinated or non-fluorinated  
7 (meth)acrylate polymer precursors, and combinations and/or derivatives of two or  
8 more of these precursors;  
9 wherein the layers of organic material alternate with the layers of inorganic material.

- 1 13. The barrier film of claim 12 wherein the total number of organic and inorganic layers
- 2 in the film is between about 100 and about 1000 layers, or between about 1000 and
- 3 about 10,000 layers, or between about 10,000 layers and about 100,000 layers.
- 1 14. The barrier film of claim 12 wherein each of the layers of inorganic material has a
- 2 thickness of about 0.1 nm to about 1 nm; about 1 to about 10 nm; or about 1 nm to
- 3 about 100 nm.
- 1 15. The barrier film of claim 14 wherein the barrier film is substantially transparent.
- 1 16. The barrier film of claim 12 wherein the barrier film has a permeability to oxygen less
- 2 than about 1 cc/m<sup>2</sup>/day, 0.1 cc/m<sup>2</sup>/day, 0.01 cc/m<sup>2</sup>/day, 10<sup>-3</sup> cc/m<sup>2</sup>/day, 10<sup>-4</sup> cc/m<sup>2</sup>/day,
- 3 10<sup>-5</sup> cc/m<sup>2</sup>/day, or 10<sup>-6</sup> cc/m<sup>2</sup>/day.
- 1 17. The barrier film of claim 16 wherein the barrier film has a permeability to water vapor
- 2 less than about 1 g/m<sup>2</sup>/day, 0.1 g/m<sup>2</sup>/day, 0.01 g/m<sup>2</sup>/day, 10<sup>-3</sup> g/m<sup>2</sup>/day, 10<sup>-4</sup> g/m<sup>2</sup>/day,
- 3 10<sup>-5</sup> g/m<sup>2</sup>/day, or 10<sup>-6</sup> g/m<sup>2</sup>/day.
- 1 18. The barrier film of claim 12 wherein one or more of the organic layers is a
- 2 superhydrophobic layer.
- 1 19. The barrier film of claim 18 wherein the superhydrophobic layer includes
- 2 fluororalkylsilane.
- 1 20. The barrier film of claim 12 wherein the organic layers are made from polymer
- 2 precursors to which one or more one or more hydrophobic groups have been added.
- 1 21. The barrier film of claim 20 wherein the one or more hydrophobic groups are selected
- 2 from the group of non-polar hydrophobic groups, methyl groups, benzyl (aromatic)
- 3 groups, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup>, SC<sub>n</sub><sup>-</sup> anions, NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup>,
- 4 Na<sup>+</sup>, Cs<sup>+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup> cations, tryptophan, isoleucine, phenylalanine,
- 5 tyrosine, leucine, valine, methionine, and alanine.
- 1 22. The barrier film of claim 12 wherein the barrier film is made from a sol including one
- 2 or more Gemini surfactants.

- 1 23. An article of manufacture, comprising:
  - 2 an object having a surface; and
  - 3 an inorganic/organic hybrid nanolaminate barrier film of the type set forth in claim 12
  - 4 disposed on the surface.
- 1 24. The article of manufacture of claim 23 wherein the object is selected from the group  
2 of optoelectronic devices, LEDs, solar cells, FETs, lasers, pharmaceutical products,  
3 tablets in packages, medical devices, food products, packaged foods, beverages,  
4 candies, display screens, touch panel displays, flat panel displays, electroluminescent  
5 windows, windows, transparent films and coatings, electronic components, and  
6 chassis for appliances used in rugged environments.

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